KEYNOTE LECTURES
PHASE DIAGRAMS, MICROSTRUCTURES AND INTERACTIONS IN ALKYL GLUCOSIDES

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Alkyl glucosides (AG) are non-ionic surfactants derived from sugar. They have some definite advantages as compared to more traditional surfactants such as good biodegradability and dermatological properties.

In this communication I will attempt to summarize our work on this interesting class of surfactants. Thus I will discuss the appearance of phase diagrams, both from binary AG/water and ternary AG/water/additive (where additive is a hydrocarbon or co-surfactant) systems. The phase diagrams have been derived from D₂O NMR experiments but also using both differential scanning calorimetry and a novel sorption calorimetric method, that allows the determination of very accurate phase diagrams in concentrated systems. The latter technique also conveys information about interactions in the investigated systems.

I will further describe the microstructure of the phases found, focusing on the connection between the microstructure and the characteristic liquid-liquid phase separation, which occurs in some AGs. The experimental technique used to determine the microstructure in solution phases is NMR diffusometry, while SAXS experiments have been used to characterize liquid crystal phases.
Organic and inorganic nanoparticles find use as paints, food additives, adhesives, dispersion colors, and UV-absorbers; in industry they play an important role in the formulation of pigments and in the production of catalysts. Furthermore, nanoparticles occur as intermediates in crystallization processes; in seawater desalination plants as well as in the washing machine these nuclei must be stabilized by suitable polymeric additives in order to prevent encrustation.

The formation of organic and inorganic nanoparticles and crystals from highly supersaturated solutions is a complex process that often proceeds via various intermediate stages [1] - and not by simple nucleation/growth processes. Precursor structures such as amorphous and/or hydrated nanoparticles may occur, which aggregate and/or dissolve before finally recrystallizing. Structural information on these intermediates is essential when developing polymers to control crystallization processes - either to achieve particles of a certain size or to prevent crystallization on surfaces [2].

We review the state of knowledge with respect to precursor structures that occur in particle formation processes from the aqueous phase. Emphasis is put on how to obtain time-resolved data by combining microscopic and scattering methods.

It will be discussed how particle formation/crystallization can be controlled by the use of polyelectrolytes, where several modes of action can be identified: (i) stabilization of the intermediate nanoparticles, (ii) prevention of recrystallization due to the effective wrapping in of the nanoparticles, (iii) impediment and modification of crystal growth by blocking the respective growing crystal surfaces. Which of these mechanisms is active depends on the type and the amount of polymer used.

References.
Construction of novel delivery vehicles toward optimization of therapeutic agent transportation and release at the desired diseased site is a challenging technology, requiring a multidisciplinary knowledge-base. Manipulation and application of fundamental colloid chemistry and particle engineering principles to modify and design delivery systems, constitutes a direction that can lead to novel biomaterials useful as delivery devices for various therapeutic or diagnostic applications. In the present communication, recent efforts of different approaches in engineering lipid-based delivery systems will be described, each focusing on improvement of a specific pharmacological obstacle before achievement of a therapeutic goal, in this way transcending from gene therapy to tumor therapeutics. First, by manipulating the surface, aggregation and flocculation behavior, and physicochemical interactions with other molecules of a genetically modified, replication-defective virus population, novel gene delivery vectors were engineered. The new molecular complexes exhibited altered biological and pharmaceutical profiles in vitro and in vivo, constituting a distinct class of gene transfer vectors. Towards a different therapeutic approach, the interaction of physicochemically different liposome systems with multicellular spheroid tumor models illustrates the effect their surface characteristics have on their intratumoral transport and diffusion, factors extremely crucial in determining the overall therapeutic efficacy of any cancer drug. Throughout those studies one fundamental issue is asserted: the opportunity to rationally design optimum delivery systems for gene therapy or other therapeutic applications by simply exercising colloid and surface engineering principles and techniques to manipulate established and powerful agents (biological, radiological, chemical) towards their transformation to effective therapeutics.
Water transportation, emulsion metastability, premature reaction between two reactive oils during storage, handling, toxicological issues, are key problems in the industry. One of the answers is from a liquid make a powder by obtaining dry emulsion.

Principle to manufacture a dry emulsion is the following: add a natural or synthetic polymer to an oil-in-water emulsion, then dry this emulsion containing additives – by spray drying for example, finally collect and store a free flowing powder. This powder is redispersible in water and the emulsion is recovered, ready for application.

Of course, dry emulsions are known since powder milk or dried aroma are used for food applications [1]. Main limitation to a larger use of these dry emulsions has been for years the limited pay load in encapsulated liquid (30%) [2]. One will show that this limitation is due to emulsion unstability upon drying. The aim of this study was to closely link physical-chemistry to process and to demonstrate how with new developments, pay load up to 65% in encapsulated liquid can be achieved [3].

Various applications are targeted for these new dry emulsions. Markets like Agrochemical are specifically developed [4].

References
INELASTIC X-RAY SCATTERING STUDY OF PHONONS IN LIQUID CRYSTALLINE DNA

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A high resolution x-ray scattering method is used to measure spectra of the collective density oscillations propagating along the axis of a rod-like supra-molecular system made of a shear-aligned columnar hexagonal liquid crystalline phase of DNA dispersed in water. The dynamic structure factor is extracted from the spectrum using a Generalized Three Eigenmode theory developed by one of us earlier. The dynamic structure factor consists of three Lorentzian lines, one central Rayleigh and two symmetrically shifted Brillouin peaks, from which the thermal diffusion coefficient, the phonon frequency and damping can be obtained. We investigated three systems: a 40 wt % calf-thymus DNA of molecular weight 8.4x10⁷ Daltons (13,000 base pairs) in water; and 40% DNA in water with 8.5 mmol of MgCl₂ and ZnCl₂ respectively added. The phonon dispersion relations obtained show an oscillatory behavior in the Q (magnitude of the scattering vector) range of 2 nm⁻¹ to 30 nm⁻¹, similar to that obtained from lipid bilayers before. The dispersion relation of 40% DNA rods in pure water, for example, starts with a linear dispersion at low q with a high-frequency sound speed of about 3100 m/s, similar to that observed in bulk water, reaching a maximum of ω = 12 meV at q = 9 nm⁻¹, going down to a valley at q = 18 nm⁻¹, coming up to a secondary (lower) maximum at q = 25 nm⁻¹ and eventually going down to zero at q = 30 nm⁻¹. One major distinctive feature of the DNA systems from liquids is that the dispersion relation in the shear aligned DNA extends to a considerably higher q than that observed in liquids. The extended range of q includes q values corresponding to that in the second Brillouin zone in a crystalline system. This latter feature implies that a DNA rod can be regarded approximately as a one-dimensional crystal, as far as the density oscillations are concerned. This signifies that one ought to be able to extract the stretching force constant of a single DNA molecule from the analysis of the dispersion relation. The details of the analyses of the three systems studied will be presented.
Interactions of lipids with proteins and low-molecular-weight lipophilic biomolecules play a significant role in many biological systems and biochemical processes. The digestion of fats, transport of lipids, and, of course, biomembranes should be considered as the prominent examples of the above statement. In biomembranes, lipids and proteins are the dominant constituents. On the average, proteins account for about half of the membrane mass in eukaryotic cells. In parallel with these biopolymers, biomembranes contain several functionally important molecules of lower molecular weight – ubiquinones, plastoquinones, lipophilic vitamins. Thus, not surprisingly, the efforts to explore the unique features of biomembranes have stimulated a considerable body of work performed on the biomimetic lipidic systems with entrapped guest-biomolecules. In this respect, there is no doubt that the reversed bicontinuous cubic ($Q_{II}$) phases of lipids are among the most elegant models of the lipid bilayer. Moreover, as pointed out in several studies, a number of cubic mesophases have been observed in conditions close to those prevailing in living organisms, and seem to be involved in different biological processes. In parallel with the biomimetic value, the $Q_{II}$ phases are also gaining in practical importance. These functionalized 3D-structures may be used as matrices for membrane protein crystallization, protein and drug delivery systems for pharmaceutical applications, and also as biocatalytically active layers in biosensors.

In our research, the principal emphasis has been on two topics:

(i). Structural features of the functionalized $Q_{II}$ phases of lipids have been studied by X-ray diffraction, Raman and FT-IR spectroscopic techniques. Among the entrapped biomolecules were: proteins lysozyme, cytochrome c and glucose oxidase; lipophilic biomolecules vitamin K$_1$ and ubiquinone-10. In these studies, the focus was on the phase types, their stability, crystallographically determined parameters, and interactions at a molecular level.

(ii). In the area of electrochemical and bioanalytical applications of the bicontinuous $Q_{II}$ phases with entrapped biomolecules, we cover amperometric and potentiometric systems. To this end, the phases were functionalized by cytochrome c, glucose and L-lactate oxidases, urease, creatinine deiminase, microperoxidase-11. All these systems were characterized in terms of macrokinetics and practical significance.
WHAT IS THE COLLOIDAL TEMPLATE ROLE IN CONTROLLING THE SIZE AND SHAPE OF NANOCRYSTALS?

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In this presentation we will discuss the role of the template to control the particle size and shape [1]. This will be based on reverse micelles and other templates. With some discrepancies, reverse micelles are a rather good candidate for controlling the size of spherical nanocrystals. However, they are not the determining factor in controlling the shape of inorganic materials. Crystal growth on the nanoscale seems to follow behavior similar to that of the bulk phase with a marked dependence on pH. The latter is particularly important when some impurities are present in the growth medium because it influences, e.g., the formation either of zwitter-ions or of complex ions, the efficiency of which is greater than that of the initial impurity. These elements lead to a decrease in the growth rates of certain crystal faces. These conclusions are based on data obtained with copper nanocrystals produced by using Cu(AOT)2-isoctane-water solution as a template. Even if the template does not change with various salt additions, the nanocrystal growth markedly depends on the salt used. It is demonstrated that chloride ions enable the growth of nanorods with an aspect ratio varying with chloride concentration. Conversely, only a slight amount of bromide ion is needed to increase the nanorod aspect ratio from 3 to 5 without any changes when increasing the bromide ion concentration. A rather large number of cubes are produced. Formations of nanorods and cubes are explained in terms of anion adsorption on (111) and (100) faces, respectively. By replacing chloride by other ions, the morphology of copper nanocrystals drastically changes. In all cases the nanocrystals formed are fcc single crystals with a polyhedral shape or crystals composed of fcc tetrahedra (deformed or not) bounded by (111) faces. Some cylinders are formed by the connection of 2 different crystals with different 5 fold axes and/or with additional planes. This gives rise to various particle shapes.

References.
SPECIFIC ION EFFECTS IN THE FORMATION OF INORGANIC COLLOIDS: INSIGHTS FROM MODEL SYSTEMS

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Specific ion effects are ubiquitous in colloid science. In recent years, with the great increase of activity in the area of colloidal (wet chemical) production of new inorganic materials, “spectator” ions have been found to play significant – and some times unexpected - roles in materials syntheses. The situation respecting the production of mesoporous solids was recently reviewed [1], but similar phenomena have been found in the production of metal or semiconductor particles. Specific ion effects are particularly important in procedures that make use of surfactants or polymers as templates, stabilizers, or habit-modifiers. Such ionic effects are closely related to the Hofmeister series of ions, which was created on the basis of salt effects on protein solubility in water [2]. The Hofmeister series appears in a wide range of chemical and biological phenomena, but its exact origin is not quite understood to date, since it stems from the interplay of ion-surface and ion-water interactions. In this presentation, I will try to make the connection between the two worlds: that of inorganic colloid production and that of specific ion effects at surfactant interfaces. To understand the basis of specific ion effects in the complex systems of inorganic colloid synthesis it is useful to consider much simpler model systems. I will discuss two model systems that are currently being exploited both experimentally and theoretically. One is the free surface of electrolyte solutions, with emphasis on the effect of electrolytes on the surface tension of water [3,4]. The other is a sequence of precisely controlled phospholipid structures (micelles, monolayers, and bilayers). The emerging picture supports the notion that specific ion effects act through binding or specific interactions at interfaces, and not through a – more or less obscure – modification of the structure of water, as was believed until recently in the biological community.

References.
Interactions in colloids and with surfaces are usually modeled with (charged) hard-sphere potentials, eventually completed with chemically mysterious Yakawa or similar potentials. Counterions or added electrolytes are supposed to modify colloidal properties via their charges and, in advanced models, via their sizes. Solvent properties are usually taken into account via the dielectric constant.

However, such simple models never can explain the specificity of ions and solvents, although the influence of ions and solvents beyond their size, charge and macroscopic dielectric constant can be huge. As long as no predictive theory is available, it is difficult to take profit of such specificities for the design of new materials.

The present contribution gives examples of specific ion and solvent effects in complex liquids, especially in colloidal and biological systems. Furthermore, the state of art of the theory of complex electrolyte systems is summarized.
PHOTO-SURFACTANTS

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For surfactants containing a suitable chromophore, light can be used to trigger changes in aggregation and adsorption. The advantage of this approach is it eliminates, or minimizes, the need for composition or temperature changes. New photosurfactants have been synthesized, and photoreactions in water, water-in-oil microemulsions, interfacial properties and changes in aggregation characterized \cite{1}. As such changes in activity under wide range of colloidally relevant situations has been demonstrated: air-water, oil-water and solid-liquid interfaces, as well as aggregation in aqueous and microemulsion dispersions. These results highlight the importance of molecular design for generating effective and efficient photosurfactants.

\begin{figure}[h]
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\includegraphics[width=0.8\textwidth]{figure.png}
\caption{Appearance, SANS data (symbols) and analysis (lines) from photo-shrinkable microemulsions.}
\end{figure}

References.
Secretory phospholipase A2 (sPLA2) refers to a large class of water-soluble interfacially active enzymes that function mainly on organized types of substrate, e.g. micelles and lipid bilayers. The activity of the enzyme is strongly controlled by the lateral organization and the physical properties of the substrate, in particular the structure in the nano-meter range. Lipid bilayers are prone to such small-scale structuring due to their intrinsic softness that implies formation of lipid domains near lipid phase transitions and in phase-separation regions. Results obtained from a variety of experimental and theoretical studies of PLA2 activity on lipid-bilayer substrates will be presented which provide insight into the biophysical mechanisms of PLA2 activation on lipid bilayers and liposomes of different composition. The insight into these mechanisms has been used to propose a novel principle for liposomal drug targeting, release, and absorption triggered by secretory PLA2.

References.
NANOSCIENCES FOR THE CONSERVATION OF CULTURAL HERITAGE

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Nanotechnology, usually portrayed as the futuristic pursuit of molecular-scale machines, has something to offer to the conservation of Cultural Heritage. As illustrative examples we report some recent methods for the restoration of works of art where microemulsions and nanoparticles of calcium hydroxide have been used to restore frescoes (Beato Angelico, Sogliani, Taddeo Gaddi, Piero della Francesca, etc.), or to de-acidify papers and canvas.